

## RHENIUM-TUNGSTEN ALLOYS

### BACKGROUND OF THE INVENTION

**[0001]** 1. Field of Invention

**[0002]** The present invention relates to a process of forming rhenium-tungsten alloys that exhibit exceptional mechanical properties and rhenium-tungsten alloys formed according to the process.

**[0003]** 2. Description of Related Art

**[0004]** Rhenium has a very high melting point (mp 3180 °C), no known ductile to brittle transition temperature, excellent chemical resistance and high electrical resistivity over a wide temperature range. It is sold in the form of foil, sheet, plate, ribbon, wire, rod and powders for use in a variety of applications, particularly in the lighting and aerospace industry.

**[0005]** Rhenium is derived primarily from the roasting of molybdenum concentrates generated in the copper mining industry. During the roasting of molybdenite, rhenium is oxidized and carried off in the flue gases. These gases are scrubbed to remove the rhenium, which is then recovered in solution using an ion exchange process. The rhenium solution is then treated and neutralized with ammonium hydroxide to precipitate ammonium perrhenate. Ammonium perrhenate can be reduced in a hydrogen atmosphere to form rhenium metal powder. The rhenium metal powder can be compacted and sintered to form high-purity rhenium metal.

**[0006]** Depending upon the raw material source and processing techniques employed, high-purity rhenium metal will typically have a rhenium content of from about 99.8% to 99.9999% by weight (on a metallic content basis). The most common trace contaminant in high-purity rhenium metal is molybdenum, but traces of other elements are sometimes also observed in high-purity rhenium metal.

**[0007]** High-purity rhenium metal has a maximum room temperature tensile strength of about 140 ksi, as tested in accordance with the ASTM E8-03 standard. Inter-granular separation has been observed in samples of high-purity rhenium metal during processing and mechanical testing. High-purity rhenium metal appears to fail in such testing at the grain boundaries.

## BRIEF SUMMARY OF THE INVENTION

[0008] The present invention provides a process of forming rhenium-tungsten alloys consisting essentially of rhenium and from about 0.025% (250 ppm) to less than about 10% by weight tungsten. The process according to the invention comprises coating rhenium metal powder with a liquid comprising a tungsten compound, drying the coated rhenium powder and then sintering the dried coated rhenium powder to obtain the rhenium-tungsten alloy. Alternatively, a liquid comprising a rhenium compound can be contacted with a liquid comprising a tungsten compound to form a mixture, which is then treated with a precipitating agent. The precipitate is then dried and sintered to obtain a rhenium-tungsten alloy.

[0009] Rhenium-tungsten alloys formed in accordance with the methods of the invention exhibit improved mechanical properties at all temperature ranges as compared to high-purity rhenium, without exhibiting a loss in ductility. The presence of the relatively small amount of tungsten in the rhenium-tungsten alloys according to the invention appears to produce an alloy having a substantially smaller grain structure than that which is observed in high-purity rhenium metal. This smaller grain structure is believed to improve the mechanical properties of the rhenium-tungsten alloys, which also improves its processability.

[0010] The foregoing and other features of the invention are hereinafter more fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principles of the present invention may be employed.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 is a photomicrograph showing the grain structure of a rhenium-tungsten alloy according to the invention.

[0012] Fig. 2 is a photomicrograph showing the grain structure of high purity rhenium metal.

[0013] Fig. 3 is a photograph showing the edge of a sheet of cold rolled rhenium and the edge of a sheet of a cold rolled rhenium-tungsten alloy.

[0014] Fig. 4 is a graph showing the longitudinal tensile stress-strain response of a cold rolled rhenium-tungsten alloy according to the invention at 70 °F in comparison to that of cold rolled high-purity rhenium metal at the same temperature.

[0015] Fig. 5 is a graph showing the longitudinal tensile stress-strain response of a cold rolled rhenium-tungsten alloy according to the invention at 2500 °F in comparison to that of cold rolled high-purity rhenium metal at the same temperature.

[0016] Fig. 6 is a graph showing the longitudinal tensile stress-strain response of a cold rolled rhenium-tungsten alloy according to the invention at 3500 °F in comparison to that of cold rolled high-purity rhenium metal at the same temperature.

#### DETAILED DESCRIPTION OF THE INVENTION

[0017] In accordance with the method of the invention, rhenium powder is contacted with a liquid comprising a tungsten compound under mixing conditions sufficient to evenly distribute the liquid throughout the rhenium powder and thereby wet all of the rhenium powder particles. The rhenium powder used in the invention can be of any particle size and shape, but preferably is minus 200 mesh rhenium flake powder. The rhenium powder is preferably very pure, such as the 99.9999% purity rhenium powder sold by Rhenium Alloys, Inc. of Elyria, Ohio, but other less pure rhenium powders can be used. Typical trace contaminants found in rhenium powders include molybdenum and/or potassium.

[0018] Ammonium metatungstate, which is soluble in water, is the preferred tungsten compound for use in the invention, but other compounds (typically tungsten salts) can be used such as, for example, ammonium paratungstate, which is also soluble in water. Ammonium metatungstate is a solid at typical room temperatures (~22.5 °C), but can be effectively combined with rhenium powder in the form of a dilute aqueous solution.

[0019] No surfactants are generally needed in order to obtain good wetting. The concentration of the tungsten compound in water or other solvent is not critical, but should be adjusted such that only enough water is used to completely wet all of the rhenium powder. Mechanical blending is sufficient to obtain a homogeneous distribution of the liquid comprising the tungsten compound and the rhenium powder.

[0020] The use of a liquid comprising a tungsten compound is necessary in order to obtain homogenous distribution of the tungsten material throughout the bulk of rhenium powder. It is not possible to obtain as even and as homogeneous a distribution of tungsten throughout the bulk of the rhenium powder by mixing tungsten powder with the rhenium powder. It is very difficult to form a homogeneous mixture of dry tungsten powders and rhenium powders due to differences in density and particle morphology. However, a liquid comprising a tungsten compound can be evenly distributed on the surface of rhenium powders, which leads to excellent homogeneity upon drying.

[0021] Once the rhenium powder has been completely wetted with the liquid comprising the tungsten compound, the coated rhenium powder must be dried. The method of drying is not critical, and drying can be accomplished by any conventional means. The bulk of the coated rhenium powder can be heated without additional mixing or, more preferably, the coated rhenium powder can be dried as it is being tumbled or mixed. Depending upon the drying method employed, some particle agglomeration may be observed. Agglomerated particles can be ground into usable powder after the drying step without disturbing or upsetting the homogeneous distribution of the materials.

[0022] The dried coated rhenium metal powder is then compacted into any desired shape. The material can be used to form products via near-net shape powder metallurgy. The material can also be consolidated using cold isostatic pressing or die compaction, which is well known. The compaction conditions used with the dried coated rhenium metal powders are the same as used in conventional powder metallurgy for high purity rhenium.

[0023] Compaction of the dried coated rhenium metal powder results in the formation of a green compact. Preferably, the green compact is pre-sintered to reduce any oxides that may be present, to reduce the tungsten compound to tungsten metal, and also provides some diffusion of the rhenium and tungsten. Pre-sintering times and temperatures are not critical, but pre-sintering at temperatures above 1,500 °C for periods of greater than twelve hours appear to provide the best results.

[0024] The pre-sintered compact is then sintered at a temperature of greater than about 2,200 °C in a reducing atmosphere or, less preferably, in a vacuum. Sintering

times should be kept at a minimum, with a sintering time of six hours typically being sufficient. Longer sintering times and higher sintering temperatures tend to produce rhenium-tungsten alloys with a larger grain structure, which is not desirable for some applications because it tends to reduce the mechanical properties of the resulting alloy.

**[0025]** After sintering, the resulting alloy can be, but need not be, further treated in the same manner as high-purity rhenium metal. Typical additional treatment steps include, for example, hot isostatic pressing (HIP), cold-rolling, swaging and other cold forming processes. The rhenium-tungsten alloys according to the invention can be formed into final products using near-net shape powder metallurgy, or into foils, sheets, plates, bars, rods, wires and ribbons using conventional processing techniques and equipment.

**[0026]** The method of the invention has heretofore been described as a solid-liquid method, wherein solid particles of rhenium are coated with a liquid comprising a tungsten compound. While this is the preferred method, it is also possible to form rhenium-tungsten alloys of the present invention via a liquid-liquid method. In the liquid-liquid method, a liquid comprising a rhenium compound such as perrhenic acid is mixed with a liquid comprising a tungsten compound such as ammonium metatungstate to obtain a mixture. A precipitating agent such as ammonium hydroxide is added to the mixture to precipitate co-rhenium/tungsten salts. The co-rhenium/tungsten salts can then be co-reduced to form a powder that is suitable for compaction and consolidation as previously described above.

**[0027]** The addition of a relatively small amount of tungsten to the rhenium surprisingly resulted in the formation of an alloy having a finer grained microstructure than that of high-purity rhenium metal. The finer grain structure is believed to be one of the reasons why the rhenium-tungsten alloys according to the invention exhibit improved mechanical properties as compared to high purity rhenium metal. For example, rhenium alloyed according to the invention with 5% tungsten by weight (Re5%W) had a room temperature tensile strength of 184 ksi with 31% elongation, as tested in accordance with the ASTM E8-03 standard. Rhenium alloyed with 2.5% tungsten by weight (Re2.5%W) had a room temperature tensile strength of 181 ksi with 37% elongation. And, rhenium alloyed with 1% tungsten by weight (Re1%W) had a

room temperature tensile strength of 171 Ksi with 44% elongation. These mechanical properties exceed that of high-purity rhenium, which has a room temperature tensile strength of 140 Ksi and an elongation of 36%.

[0028] A loss of ductility was observed as the tungsten content of the alloy approached 10% by weight. Accordingly, an amount of tungsten less than about 10% by weight preferred in order to obtain the desired improvements in mechanical strength without losing ductility. More preferably, the tungsten content of the alloys is from about 0.025% to about 5% by weight, or about 0.05% to about 2.5% by weight, or about 0.06% to about 1.25% by weight. A rhenium-tungsten alloy formed according to the present invention having a tungsten content of about 0.067% by weight is particularly preferred.

[0029] As noted above, the substantial improvements observed in the mechanical properties of the alloys according to the invention was not expected. Several phase diagrams of the binary tungsten-rhenium system have been published over the years, but none included data points in the area of present interest. Furthermore, prior art binary tungsten-rhenium phase diagrams were based upon alloys that were formed by arc-melting rhenium and tungsten together. Applicants have found that the desired improvements in mechanical properties provided by the rhenium-tungsten alloys of the present invention cannot be obtained by arc-melting the relative amounts of rhenium and tungsten together to form an alloy. Reasons for this phenomenon include the difficulty of obtaining good dispersion of the tungsten throughout the bulk of the rhenium and the formation of very large grain structures at arc melting temperatures.

[0030] Rhenium-tungsten alloys according to the present invention can be processed substantially more easily than conventional high-purity rhenium metal. One particularly desirable processing improvement is in the area of drawn wire, which is used as filaments in some lighting applications. Thus, the present invention provides wire formed of rhenium-tungsten alloys formed in accordance with the process of the invention.

[0031] In addition to wire, rhenium-tungsten alloys of the present invention are also suitable for use in the fabrication of rocket engines, in heat shielding and in element packages for high temperature furnaces. Other applications include hot valve

assemblies. Rhenium-tungsten alloys according to the invention can be used in virtually any application where higher strength rhenium is desired.

[0032] It is believed that rhenium can be alloyed with other metals such as, for example, molybdenum, tantalum, iridium, ruthenium and osmium, by coating a metal powder consisting essentially of rhenium with a liquid comprising a compound of such metals, drying the coated rhenium powder, compressing the coated powder to form a compact and sintering the compact to form an alloy. Similarly, it is believed that rhenium can be alloyed with such metals by providing a precipitate comprising a rhenium compound and a compound of such metals, compressing the precipitate to form a compact and sintering the compact to form the alloy.

[0033] The following examples are intended only to illustrate the invention and should not be construed as imposing limitations upon the claims.

#### EXAMPLE 1

[0034] Six separate 200 gram portions of 99.9999% purity rhenium powder flakes (-200 mesh) obtained from Rhenium Alloys, Inc. of Elyria, Ohio were placed into separate beakers marked A, B, C, D, E and F, respectively. Ammonium metatungstate was dissolved in deionized distilled water and then added to the beakers labeled A, B, C, D, E and F, respectively, to provide the final concentration of tungsten shown in weight percent in Table 1 below. Additional water was added to each beaker, as necessary, to insure good wetting of the rhenium powders and good distribution of the tungsten compound throughout the powders. The contents of each beaker were stirred together until the liquid coated the powder particles uniformly. A control sample comprising the 200 grams of the same rhenium powder and distilled water (no tungsten compound was added) was placed in a beaker marked Control.

[0035] The beakers containing the wetted powders were placed on a hot plate and the volatile portion of the liquid was driven off. Two 80 gram samples were taken from each beaker and die compacted using a 90 ton hydraulic press to obtain green compacts of about 2.53 inches in length, about 0.61 inches in width and about 0.28 inches in height. The actual density of the compacts was determined to be about 53% of theoretical density.

[0036] The green compacts were pre-sintered at 1400 °C for 20 minutes. After pre-sintering, the pre-sintered compacts were about 2.35 inches in length, 0.57 inches in width and about 0.26 inches in height. The actual density of the green compacts was determined to be 65% of theoretical density.

[0037] The pre-sintered compacts were then sintered in a hydrogen atmosphere at 2350 °C for four hours to form test bars. The test bars were allowed to cool to room temperature in the hydrogen atmosphere. The test bars had a length of about 2.06 inches, a width of about 0.49 inches and a height of about 0.23 inches. The actual density of the test bars was about 97.5% of theoretical density.

[0038] Each of the test bars was then repeatedly cold rolled and annealed using conventional rhenium metal processing techniques to form sheets about .080 inches thick. The sheets were EDM cut to form sub-size tensile bars in accordance with the procedures set forth in the ASTM E8-03 standard. The results of room temperature tensile testing in accordance with the ASTM E8-03 standard are reported in Table 1 below (where: "Re%" means weight percent rhenium; "W%" means weight percent tungsten; "RT TS" means room temperature (70°F) tensile strength as measured in accordance with ASTM E8-03; "RT YS" means room temperature (70°F) yield strength as measured in accordance with ASTM E8-03; and RT Elong% means room temperature (70°F) percent elongation as measured in accordance with ASTM E8-03).

Table 1

	<u>Control</u>	A	B	C	D	E	F
Re%	100	99.95	99.5	99.0	97.5	95.0	90.0
W%	.0	0.05	0.5	1.0	2.5	5.0	10.0
RT TS	140	153	158	171	181	183	181
RT YS	47	77	79	86	94	92	143
RT Elong%	36	49	38	44	33	37	6

[0039] Table 1 shows that the rhenium-tungsten alloys according to the invention exhibit improved tensile strength and increased the yield strength as compared to high-purity rhenium, while maintaining the ductility of the material until the tungsten content of the alloy approaches 10% by weight. Fig. 1 is a photomicrograph showing that the

ASTM E112-96e2 grain size of tensile bar C (Re1%W) is 7. Fig. 2 is a photomicrograph showing that the ASTM E112-96e2 grain size of the Control tensile bar is 4. At all tungsten concentrations, the grain structure of the rhenium-tungsten alloy according to the invention was much smaller than that of high-purity rhenium.

[0040] In addition to the improvements in mechanical properties, an increase in end product yield can be expected because the rhenium-tungsten alloys produce less edge cracking. Fig. 3 is a photograph that shows the edges of sheets from which tensile bar F (top) and tensile bar C (bottom) were cut. Edge cracking is significantly more pronounced in tensile bar F (top), which was alloyed with 10% by weight tungsten, than tensile bar C (bottom), which was alloyed with only 1% by weight tungsten.

## EXAMPLE 2

[0041] An 0.080 inch thick sheet of a rhenium-tungsten alloy containing 1% tungsten by weight (Re1%W) was formed using the materials and procedures described in Example 1. Tensile bars were cut from the sheet in accordance with ASTM E8-03 and ASTM E21-03a. Tensile bars were tested at room temperature (70 °F), at 2500 °F and at 3500 °F. Fig. 4 is a graph of the longitudinal tensile stress-strain response of the Re1%W alloy (solid line) as compared to that of high-purity rhenium metal (dashed line) at room temperature. Fig. 5 is a graph of the longitudinal tensile stress-strain response of the Re1%W alloy (solid line) as compared to that of high-purity rhenium metal (dashed line) at 2500 °F. Fig. 6 is a graph of the longitudinal tensile stress-strain response of the Re1%W alloy (solid line) as compared to that of high-purity rhenium metal (dashed line) at 3500 °F. As shown in the graphs, the Re1%W alloy exhibited a higher longitudinal tensile stress-strain response than high-purity rhenium at all three temperatures.

[0042] Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and illustrative examples shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.